

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-124710

(43)Date of publication of application : 13.05.1997

(51)Int.Cl.

C08F 2/10  
A61L 15/60  
C08F 6/00  
C08F 20/06

(21)Application number : 07-286263

(71)Applicant :

NIPPON SHOKUBAI CO LTD

(22)Date of filing : 02.11.1995

(72)Inventor :

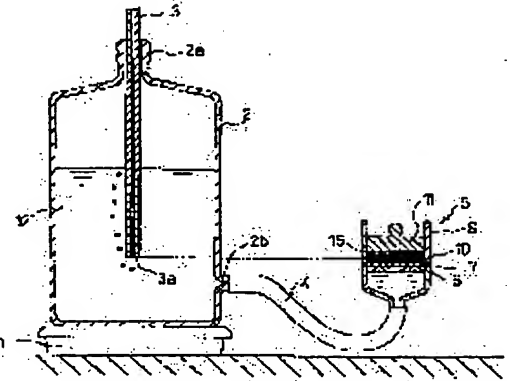
YANASE TORU  
KIMURA KAZUKI  
NAGASUNA KINYA  
SHIOJI NAOTAKE

## (54) WATER-ABSORBING RESIN AND PRODUCTION THEREOF

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a water-absorbing resin which is excellent in water absorption ratio both under normal pressure and under a high pressure and also excellent in urine resistance.

**SOLUTION:** This water-absorbing resin is obtd. by subjecting a hydrophilic unsatd. monomre (e.g. an acrylic acid-sodium acrylate mixture) to water-base soln. polymn. in the presence of an internal cross-linker and a phosphite, mixing the resultant water-absorbing resin precursor with a surface cross-tinker having groups reactive with carboxyl groups of the precursor, and heating the resultant mixture. The resin absorbs 36 g/g or higher physiological saline under normal pressure and 24g/g or higher under a high pressure and has a flow rate (16hr after absorbing artificial urine) of 1mm/min or lower. The physiological saline absorption under a high pressure is measured with an apparatus comprising a balance 1, a vessel 2, an outside-air intake pipe 3, a tube 4, a glass filter 6, and a measuring section 5.



## LEGAL STATUS

[Date of request for examination]

10.10.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3606966

[Date of registration]

15.10.2004

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

**Japanese Unexamined Patent Publication  
No. 179008/1991 (Tokukaihei 9-124710)**

A. Relevance of the Above-identified Document

The following is a partial English translation of exemplary portions of non-English language information that may be relevant to the issue of patentability of the claims of the present application.

B. Translation of the Relevant Passages of the Document

See also the attached English Abstract.

[Title of the Invention]

WATER ABSORBING RESIN AND PRODUCTION METHOD  
THEREOF

[Claims]

[Claim 1]

A production method of a water-absorbing resin, comprising the steps of (i) performing, in the presence of internal cross-linking agent and phosphorous acid and/or its salt, aqueous polymerization using a hydrophilic unsaturated monomer so as to produce a water-absorbing resin precursor, the hydrophilic unsaturated monomer mainly containing acrylic acid and/or its alkali metal salt, and (ii) adding, to the water-absorbing resin precursor, a surface cross-linking agent that is reactive with a carboxyl group contained in the water-absorbing resin precursor,

and treating the mixture with heat.

[Claim 2]

The production method as set forth in Claim 1, wherein the internal cross-linking agent is used within the range of from 0.02 mol% to 3 mol% with respect to the hydrophilic unsaturated monomer.

[Claim 3]

The production method as set forth in one of Claims 1 and 2, wherein the phosphorous acid and/or its salt is used within the range of from 0.01 % to 5 % by weight with respect to the hydrophilic unsaturated monomer.

[Claim 4]

The production method as set forth in any one of Claims 1, 2 and 3, comprising the step of performing the aqueous polymerization using persulfate.

[Claim 5]

A water-absorbing resin, having (i) an absorbency of 36g/g or greater with respect to physiological saline under no pressure, (ii) an absorbency of 24g/g or greater with respect to physiological saline under high pressure, and (iii) a flow rate of 1 mm/min or less at a time after 16 hours have passed since artificial urine was absorbed.

[Detailed description of the invention]

[0001]

[Industrial field of the invention]      The present invention relates to a water-absorbing resin and a production method thereof. In particular, the present invention relates to a water-absorbing resin that is (i) excellent in absorbing ability both under no pressure and under high pressure, (ii) excellent in urine-resistibility, and (iii) is especially suitable for sanitary material. The present invention also relates to a production method of the water-absorbing resin.

[0002]

[Prior art] In recent years, water-absorbing resin has been widely used for various purposes, not only for sanitary material (e.g., paper diapers, sanitary napkins) but also for medical use (e.g., body fluids absorbing material), for civil engineering and construction (e.g., sealing member (water-shutoff member), dew condensation preventor), for food (e.g., freshness-keeping agent), for industry (e.g., dehydrating agent for eliminating water from solvent), or agriculture and gardening (e.g., greenery). A variety of water-absorbing resins suitable for the respective purposes have been suggested.

[0003]      However, ordinary water-absorbing resin has inferior water absorbency under pressure, although its

absorbency under no pressure is high. Therefore, the water-absorbing resin cannot provide sufficient absorbency in the case where the water-absorbing resin is used for water-absorbing material on which high load is to be applied while being used (e.g., a paper diaper for adults that has been increasingly demanded in recent years). Accordingly, there has been a demand for resin that exhibits excellent absorbency under pressure, especially under high pressure, while maintaining high absorbency under no pressure.

[0004] Further, with respect to pure water and physiological saline, ordinary water-absorbing resin constantly exhibits high absorbency for a long period of time. However, with respect to urine, it has been known that the ordinary water-absorbing resin exhibits a unique phenomenon. Specifically, a gel that has absorbed urine and therefore has swelled is deteriorated and destroyed as time passes by. Therefore, in order to utilize the water-absorbing resin as a water-absorbing material (e.g., paper diapers), it is strongly demanded that the durability of swelled gel having absorbed urine is improved while excellent absorbencies both under no pressure and under high pressure are maintained.

[0005] One method of improving the resistance (the durability will be referred to as urine-resistibility hereinafter) of the water-absorbing resin against urine is a

method in which the amount of cross-linking agent to be used in polymerization is increased so as to increase the cross-linking density of the water-absorbing resin. This method, however, requires high production costs and only produces a water-absorbing resin that exhibits significantly reduced absorbency under no pressure.

[0006] There has been suggested another method of improving the urine-resistibility of the water-absorbing resin. Specifically, a particular additive is added to the water-absorbing resin. Examples of the additives include: an oxygen-containing reducing inorganic salt (Japanese Unexamined Patent Publication No. 63-118375, U.S. Patent No. 4863989, U.S. Patent No. 4972019); an anti-oxidant (Japanese Unexamined Patent Publication No. 63-127754); an oxidant (Japanese Unexamined Patent Publication No. 63-153060); and reductant containing sulfur (Japanese Unexamined Patent Publication No. 63-272349). However, regardless of which one of the additives is used, the urine-resistibility and handiness cannot be improved to a satisfactory level. Moreover, the absorbency, both under no pressure and under high pressure, of the water-absorbing resin decreases.

[0007] Further, there has been suggested another method of improving the urine-resistibility of the water-absorbing resin. Specifically, a particular compound is added during polymerization. Examples of the above

method include: polymerization performed in the presence of a particular amount of chain transfer agent and a particular amount of cross-linking agent (Japanese Unexamined Patent Publication No. 2-255804, Japanese Unexamined Patent Publication No. 3-179008, EP Patent No. 0372981), polymerization performed in the presence of hypophosphorus compound (Japanese Unexamined Patent Publication No. 2-300210), and polymerization performed in the presence of water-soluble phosphoric acid type compound (Japanese Unexamined Patent Publication No. 5-97929).

[0008]

[Problem to be solved by the invention] These methods can improve the urine-resistibility of the water-absorbing resin. However, none of the methods can provide a water-absorbing resin that exhibits high absorbency under high pressure.

[0009] Thus, the conventional water-absorbing resin is inferior in at least one of the absorbency under no pressure, the absorbency under high pressure, and urine-resistibility. Therefore, it has not been realized a water-absorbing resin that is excellent in the absorbency under no pressure, the absorbency under high pressure, and urine-resistibility.

[0010] For this reason, there has been a demand for a water-absorbing resin that is excellent in all of (i) the

absorbency under no pressure, (ii) the absorbency under high pressure, and (iii) the urine-resistibility. Furthermore, a production method of the water-absorbing resin has also been demanded. In other words, the present invention is in view of the above conventional problems, and has as an object to provide a water-absorbing resin that is excellent in absorbency, both under no pressure and under high pressure, and in urine-resistibility. The present invention has another object to provide a production method of the water-absorbing resin.

[0011]

[Means for solving problem] In order to achieve the above objects, the inventors of the present application have diligently researched a water-absorbing resin and a production method thereof. As a result, the inventors found that a water-absorbing resin excellent in absorbency, both under no pressure and under high pressure, and in urine-resistibility can be produced by (i) performing, in the presence of internal cross-linking agent and phosphorous acid and/or its salt, aqueous polymerization using a hydrophilic unsaturated monomer so as to produce a water-absorbing resin precursor, the hydrophilic unsaturated monomer mainly containing acrylic acid and/or its alkali metal salt, (ii) adding, to the water-absorbing resin precursor, a surface cross-linking agent that is reactive with a carboxyl group contained in



the water-absorbing resin precursor, and treating the mixture with heat. Finally, the present invention was completed.

[0012] That is, in order to solve the above problems, the invention of Claim 1, which is a production method of a water-absorbing resin, is adapted so that the production method of a water-absorbing resin includes the steps of (i) performing, in the presence of internal cross-linking agent and phosphorous acid and/or its salt, aqueous polymerization using a hydrophilic unsaturated monomer mainly containing acrylic acid and/or its alkali metal salt so as to produce a water-absorbing resin precursor, and (ii) adding, to the water-absorbing resin precursor, a surface cross-linking agent that is reactive with a carboxyl group contained in the water-absorbing resin precursor, and treating with heat.

[0013] In order to solve the above problems, the invention of Claim 2, which sets forth a production method of a water-absorbing resin, is adapted so that, in the production method of Claim 1, the internal cross-linking agent is used within the range of from 0.02 mol% to 3 mol% with respect to the hydrophilic unsaturated monomer.

[0014] In order to solve the above problems, the invention of Claim 3, which sets forth a production method of a water-absorbing resin, is adapted so that, in

the production method of one of Claims 1 and 2, the phosphorous acid and/or its salt is used within the range of from 0.01 % to 5 % by weight with respect to the hydrophilic unsaturated monomer.

[0015] In order to solve the above problems, the invention of Claim 4, which sets forth a production method of a water-absorbing resin, is adapted so that the production method of one of Claims 1, 2, and 3 includes the step of performing the aqueous polymerization using persulfate.

[0016] The above method enables to produce a water-absorbing resin that is excellent in absorbency, both under no pressure and under high pressure, and in urine-resistibility.

[0017] Further, in order to solve the above problems, the water-absorbing resin of the invention as set forth in Claim 5 is adapted so that (i) the physiological saline has an absorbency 36g/g or greater under no pressure of and an absorbency of 24 g/g or greater under high pressure and (ii) a flow rate of 1 mm/min or lower at a time 16 hours have passed since artificial urine was absorbed.

[0018] With the above arrangement, the water-absorbing resin can become excellent in absorbency, both under no pressure and under high pressure. Moreover, the water-absorbing resin is excellent in urine-resistibility. Therefore, the water-absorbing resin is

suitable for paper diapers for babies or sanitary napkins. Further, the water-absorbing resin can be utilized for sanitary material (e.g., diapers for adults) on which high load is to be applied, which sanitary material has been increasingly demanded in the recent years.

[0019] The following describes the present invention in detail. In the present invention, the absorbency under no pressure means an absorbency of water-absorbing resin with respect to physiological saline, which absorbency is measured under the condition where no pressure is being applied to the water-absorbing resin. The method of measuring the absorbency under no pressure will be specifically described in the Examples below.

[0020] On the other hand, in the present invention, the absorbency under high pressure means an absorbency of water-absorbing resin, which absorbency is measured under the condition where a pressure of, for example, 50 g/cm<sup>2</sup> is being applied to the water-absorbing resin. The method of measuring the absorbency under high pressure will be specifically described in the Examples below.

[0021] Further, in the present invention, the flow rate after artificial urine absorption is used to evaluate the level of liquidification of the hydrate gel the flow rate after artificial urine absorption. The flow rate the flow rate after artificial urine absorption is calculated on the basis of a flow rate at a time when (i) a predetermined amount of

artificial urine has been absorbed by the water-absorbing resin, and (ii) hydrate gel that is swelled to a predetermined magnification has been left under a predetermined condition for a predetermined period of time (e.g., 16 hours). The flow rate means a distance the hydrate gel moves in a unit of time while the container containing the hydrate gel is being leaned. Further, the artificial urine is an aqueous solution in which urea, sodium chloride, magnesium sulfate, calcium chloride, and L-ascorbic acid are dissolved in such a way that the respective ratios thereof are approximately equal to that in natural urine. By using the flow rate at the time when the artificial urine has been absorbed, the urine-resistibility of the water-absorbing resin is evaluated. Specifically, if the flow rate at the time when the artificial urine has been absorbed is fast, then it is determined that the water-absorbing resin is significantly deteriorated by the artificial urine and therefore is inferior in urine-resistibility. The method of measuring the flow rate at the time when the artificial urine has been absorbed will be specifically described in the Examples below.

[0022] The water-absorbing resin according to the present invention is produced by (i) synthesizing a particular water-absorbing resin precursor and (ii) treating the water-absorbing resin precursor with heat in

the presence of surface cross-linking agent. The water-absorbing resin precursor is produced by aqueous polymerization using hydrophilic unsaturated monomer in the presence of internal cross-linking agent and phosphorous acid and/or its salt.

[0023] The hydrophilic unsaturated monomer (the hydrophilic unsaturated monomer will be referred to as a monomer hereinafter) contains acrylic acid and/or its alkali metal salt as its main component. In order to further improve the absorbency of the water-absorbing resin, it is preferable that the acrylic acid content and its alkali metal salt content in the monomer be 70 mol% or greater, or more preferably, 90 mol% or greater.

[0024] In order to further improve the absorbency of the water-absorbing resin, it is preferable that the alkali metal salt content in acrylic acid with respect to the total amount of acrylic acid and its alkali metal salt be 30 mol% or greater, or more preferably, in the range of from 50 mol% to 80 mol%.

[0025] The monomer may contain, when necessary, an unsaturated monomer other than the acrylic acid. The monomer other than acrylic acid is not particularly limited. Concrete examples of the monomer other than acrylic acid include: anionic unsaturated monomers (and their salts) such as methacrylic acid, maleic acid, vinyl sulfonic acid, stylenesulfonic acid,

2-(meth)acrylamide-2-methylpropanesulfonic acid,  
2-(meth)acryloylethanesulfonic acid,  
2-(meth)acryloylpropanesulfonic acid, and the like;  
non-ionic hydrophilic group containing unsaturated  
monomers such as (meth)acryl amide,  
N-ethyl(meth)acrylamide, N-n-propyl(meth)acrylamide,  
N-isopropyl(meth)acrylamide,  
N,N-dimethyl(meth)acrylamide,  
2-hydroxyethyl(meth)acrylate,  
2-hydroxypropyl(meth)acrylate,  
methoxypolyethyleneglycol(meth)acrylate,  
polyethyleneglycolmono(meth)acrylate, vinylpyridine,  
N-vinylpyrrolidone, N-acryloylpiperidine,  
N-acryloylpyrrolidine, and the like; and  
cationic unsaturated monomers such as  
N,N-dimethylaminoethyl(meth)acrylate,  
N,N-diethylaminoethyl(meth)acrylate,  
N,N-dimethylaminopropyl(meth)acrylate,  
N,N-dimethylaminopropyl(meth)acrylamide, and their  
quaternary salts. In a case where a monomer other than  
acrylic acid is used, the monomer content is preferably  
30mol% or less, and more preferably 10mol% or less.

[0026] The internal cross-linking agent used in the  
aqueous polymerization using the monomer is a compound  
containing a plurality of polymerizable unsaturated  
groups or a plurality of reactive groups. Examples of the

internal cross-linking agent (B) includes:  
N,N'-methylenebis(meth)acrylamide,  
(poly)ethyleneglycoldi(meth)acrylate,  
(poly)propyleneglycoldi(meth)acrylate,  
trimethylolpropanedi(meth)acrylate,  
trimethylolpropanetri(meth)acrylate,  
glycerictri(meth)acrylate,  
glycericacrylatemethacrylate, ethyleneoxide denatured  
trimethylolpropanetri(meth)acrylate,  
pentaerythritoltetra(meth)acrylate,  
dipentaerythritolhexa(meth)acrylate,  
triallylcyanurate, triallylisocyanurate, triallylphosphate,  
triallylamine, poly(meth)allyloxyalkanes,  
(poly)ethyleneglycoldiglycidylether, glyceroldiglycidylether,  
ethyleneglycol, polyethyleneglycol, propyleneglycol,  
glycerin, pentaerythritol, ethylenediamine,  
polyethyleneimine, glycidyl(meth)acrylate and the like.  
These internal cross-linking agents may be used solely or  
in a suitable combination. It is more preferable that a  
compound, among the above exemplified compounds,  
having a plurality of polymerizable unsaturated groups be  
used as the internal cross-linking agent.

[0027] It is preferable that the internal cross-linking  
agent content with respect to the total amount of the  
above monomer be in the range of from 0.02 mol% to 3  
mol%, or more preferably in the range of from 0.05 mol%

to 1.5 mol%. It is not preferable that the internal cross-linking agent content be less than 0.02 mol% because, in this case, a component that can be dissolved into water increases. In other words, a water-soluble component increases. Moreover, the swelled gel having absorbed water becomes slimier. Therefore, in the case where the swelled gel is used in, for example, diapers, not only uncomfortable feeling is provided to the user, but also the urine-resistibility is degraded. On the other hand, it is not preferable that the internal cross-linking agent content be more than 3 mol%, because, in this case, the absorbency of the water-absorbing resin precursor under no pressure decreases significantly, and consequently, both the absorbency of water-absorbing resin under no pressure and the absorbency of water-absorbency resin under high pressure decrease.

[0028] In the present invention, phosphorous acid and/or its salt (this will be referred to as phosphorous acid (salt) hereinafter) that is used for aqueous polymerization using the monomer is not particularly limited, as long as it is soluble to water or aqueous solution of monomer. Examples of the phosphorous acid (salt) include: phosphorous acid; normal salt of phosphorous acid, such as disodium phosphite, dipotassium phosphite, ammonium phosphite; and acid salt of phosphorous acid, such as sodium hydrogen



phosphite, potassium hydrogen phosphite, ammonium hydrogen phosphite. Among the phosphorous acid (salt) listed above, disodium phosphite, dipotassium phosphite, and sodium hydrogen phosphite are especially preferable. These phosphorous acid (salt) may be used either solely or in combination of thereof. Further, two or more of the above may be mixed at an arbitrary ratio. Phosphite of cation having a valence of two or greater, such as calcium or barium, is not preferable because such phosphite is usually insoluble to water.

[0029] It is preferable that the dosage of the phosphorous acid (salt) be in the range of from 0.01% by weight to 5% by weight with respect to the monomer, or more preferably in the range of from 0.1% by weight to 2% by weight. In the case where the dosage of the phosphorous acid (salt) is less than 0.01% by weight, the absorbency of the water-absorbing resin precursor under no pressure becomes low, and the absorbency of the water-absorbing resin under no pressure and the absorbency of the water-absorbing resin under high pressure also become low. Therefore, this case is not preferable. On the other hand, in the case where the dosage of the phosphorous acid (salt) exceeds 5% by weight, the water-soluble content of produced water-absorbing resin increases significantly. This causes uncomfortable feelings when used in, for example, diapers.

Moreover, the urine-resistibility and the absorbency under high pressure are reduced. Therefore, this case is not preferable, either.

[0030] In the present invention, aqueous polymerization is employed to polymerize a monomer in the presence of an internal cross-linking agent and phosphorous acid (salt) so as to produce the water-absorbing resin precursor. In order to perform the aqueous polymerization, a conventionally-known method can be employed. Examples of the conventionally-known method include: casting polymerization in which the polymerization is performed in a cast; performing a polymerization on a belt-conveyer; performing a polymerization with an apparatus having a stirring blade (e.g., kneader) by fragmenting the generated hydrate gel polymer. Among the methods listed above, it is especially preferable to polymerize with an apparatus having a stirring blade by fragmenting the polymer because (i) it is easy to remove heat generated during the polymerization and (ii) the polymerization is performed uniformly. The apparatus having a stirring blade is not particularly limited. Examples of the apparatus include: a single-armed mixing apparatus; a single-screwed extruder, a two-armed kneader, and a three-armed kneader. Among these apparatuses, it is especially preferable to use the two-armed kneader.

[0031] The method for mixing the monomer, the internal cross-linking agent, and phosphorous acid (salt) during the aqueous polymerization is not particularly limited. For example, the internal cross-linking agent and the phosphorous acid (salt) may be mixed directly, and thereafter the solution of the mixture may be mixed with either the monomer or an aqueous solution thereof. Alternatively, the internal cross-linking agent and an aqueous solution of the phosphorous acid (salt) may be mixed, and thereafter the solution of the mixture may be mixed with either the monomer or an aqueous solution thereof. Furthermore, the internal cross-linking agent, the phosphorous acid (salt), and a part of monomer or a part of aqueous solution thereof may be mixed, and thereafter the mixed solution may be mixed with either the rest of the monomer or the rest of the aqueous solution thereof. Furthermore, the internal cross-linking agent, the aqueous solution of phosphorous acid (salt), either a part of monomer or a part of aqueous solution of the monomer may be mixed, and thereafter the mixed solution may be mixed with either the rest of the monomer or the rest of the aqueous solution thereof.

[0032] The concentration of the monomer in the aqueous solution during the aqueous polymerization using the monomer in the presence of internal cross-linking agent and phosphorous acid (salt) is not particularly limited,

but it is preferable that the concentration be between 20 % by weight and the saturation concentration, inclusive.

[0033] To start the aqueous polymerization, a radical polymerization initiator (e.g., potassium persulfate, ammonium persulfate, sodium persulfate, t-butylhydroperoxide, hydrogen peroxide, or 2,2'-azobis(2-amizino propane) dihydrochloride) may be utilized, for example. Alternatively, active energy rays (e.g., ultraviolet rays, electron rays) may be utilized. Among the examples listed above, it is especially preferable to use persulfate such as potassium persulfate, ammonium persulfate, sodium persulfate and the like. Further, in the case where an oxidizing radical polymerization initiator is used, redox polymerization may be performed by using a combination of reductants (e.g., sodium sulfite, sodium hydrogen sulfite, iron sulfate, L-ascorbic acid). It is preferable that the polymerization initiator content be in the range of from 0.001 mol% to 2 mol%, or more preferably in the range of from 0.01 mol% to 0.5 mol%.

[0034] A hydrophilic polymer (e.g., starch, cellulose, polyvinyl alcohol, polyethyleneglycol, polyacrylic acid (salts)-based cross-linking agent) may be added during the aqueous polymerization. Further, the aqueous polymerization may be performed in the presence of fabric material or an inorganic substance so as to generate a

water-absorbing complex.

[0035] The hydrate gel polymer produced by the aqueous polymerization can be used as a water-absorbing resin precursor as the way it is. However, if the amount of solid content is little, it is preferable that the hydrate gel polymer be dried further. A method of drying the hydrate gel polymer is not particularly limited, and a publicly-known drying method can be employed. Examples of the publicly-known drying method include: heated-air drying; ultraviolet-ray drying; microwave drying; drum-dryer drying; azeotropic dehydration in a hydrophobic organic solvent; and the like. It is preferable that the polymer be dried such that the dried polymer, that is, the water-absorbing resin precursor consequently contains the solid parts of 60% by weight or greater, or more preferably 90% by weight or greater. The conditions for drying, therefore, should be arranged such that the solid parts of the water-absorbing resin precursor falls into the above range.

[0036] The water-absorbing resin precursor produced by the aqueous polymerization or the water-absorbing resin precursor that is produced by the aqueous polymerization and then is dried may be pulverized or integrated so as to adjust its particle size. The average particle diameter of the water-absorbing resin precursor is not particularly limited, but it is preferable that the

average particle diameter be in the range of from 10  $\mu\text{m}$  to 2000  $\mu\text{m}$ , or more preferably in the range of from 100  $\mu\text{m}$  to 1000  $\mu\text{m}$ . It is further preferable that the average particle diameter be in the range of from 300  $\mu\text{m}$  to 600  $\mu\text{m}$ . Further, it is preferable that the particle size distribution of the water-absorbing resin precursor be narrow. By adjusting the particle size of the water-absorbing resin precursor to fall into the above range, the absorbency can be improved. Note that water-absorbing resin precursor may be in various shapes including spherical shape, ramentum shape, irregular and pulverized shape, and granular shape.

[0037] The water-absorbing resin precursor produced by the methods described above has some degree of absorbency under no pressure, absorbency under high pressure, and urine-resistibility. However, none of the absorbency under no pressure, the absorbency under high pressure, and the urine-resistibility is in the preferable ranges according to the present invention. Therefore, in order to produce a water-absorbing resin that exhibits (i) high absorbency under no pressure, (ii) high absorbency under high pressure, and (iii) excellent urine-resistibility, it is necessary to increase, by using a surface cross-linking agent, the cross-linking density in the vicinity of the surface of the water-absorbing resin precursor so that the cross-linking density of the surface

becomes greater than the internal cross-linking density. In other words, the water-absorbing resin of the present invention is produced by mixing (i) the water-absorbing resin precursor produced by the aqueous polymerization described above and (ii) a surface cross-linking agent that is reactive with the carboxyl group contained in the water-absorbing resin precursor, and thereafter heating the mixture.

[0038] Examples of the surface cross-linking agent include: polyhydroxy alcohols such as ethyleneglycol, propyleneglycol, glycerin, pentaerythritol, sorbitol, diethyleneglycol, triethyleneglycol, tetraethyleneglycol, dipropyleneglycol, tripropyleneglycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,4-pentanediol, 1,6-hexanediol, 2,5-hexanediol, trimethylolpropane, and the like; multivalent epoxy compounds such as ethyleneglycoldiglycidylether, polyethyleneglycoldiglycidylether, diglycerolpolyglycidylether, polyglycerolpolyglycidylether, propyleneglycoldiglycidylether, polypropyleneglycoldiglycidylether, and the like; multivalent amines such as diethanolamine, triethanolamine, ethylenediamine, diethylenetriamine, triethylenetetramine, and the like; multivalent isocyanate compounds such as 2,4-tolylenediisocyanate, hexamethylenediisocyanate, and

the like; ethylene carbonate (1,3-dioxolan-2-one), propylene carbonate (4-methyl-1,3-dioxolan-2-one), 4,5-dimethyl-1,3-dioxolan-2-one, epichlorohydrin, epibromohydrin, and the like. The surface cross-linking agent, however, is not limited to the compounds listed above. The polyhydroxy alcohols or multivalent epoxy compounds among the compounds listed above are especially preferable because any of them can improve the absorbency of the water-absorbing resin. These surface cross-linking agents may be used solely or in combination.

[0039] It is preferable that the amount of the surface cross-linking agent to be used be in the range of from 0.001 parts by weight to 5 parts by weight with respect to 100 parts by weight of the solid parts of the water-absorbing resin precursor, or more preferably in the range of from 0.01 parts by weight to 2 parts by weight, although the preferable amount depends upon which compound or which combination of compounds is used. By using the surface cross-linking agent listed above, the cross-linking density in the vicinity of the surface of the water-absorbing resin precursor (i.e., water-absorbing resin) can be greater than the internal cross-linking density. It is not preferable to use more than 5 parts by weight of surface cross-linking agent because (i) it is not economical and (ii) this amount is excess for forming an optimum cross-linking structure in the water-absorbing



resin. Further, it is also not preferable to use less than 0.001 parts by weight of surface cross-linking agent because, in this case, it is difficult to upgrade the properties, such as the urine-resistibility or the absorbency under high pressure, of the water-absorbing resin.

[0040] In mixing the water-absorbing resin precursor and the surface cross-linking agent, it is preferable to use water as a solvent. It is preferable that the amount of water to be used be greater than 0 and equal to or less than 20 parts by weight with respect to 100 parts by weight of the solid parts of the water-absorbing resin precursor, or more preferably in the range of from 0.5 parts by weight to 10 parts by weight, although the preferable amount depends upon, for example, the type or the particle diameter of the water-absorbing resin precursor.

[0041] Further, if necessary, a hydrophilic organic solvent may be added as a solvent when the water-absorbing resin precursor and the surface cross-linking agent are mixed. Examples of the hydrophilic organic solvent include: lower alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, and the like; ketones such as acetone and the like; ethers such as dioxane, tetrahydrofuran, and the

like; amides such as N,N-dimethylformamide and the like; sulfoxides such as dimethylsulfoxide and the like; and the like. An amount of the hydrophilic organic solvent to be added is preferably not more than 20 parts by weight, and more preferably in the range of from 0.1 parts by weight to 10 parts by weight, with respect to 100 parts by weight of a solid parts of the water-absorbing resin precursor, although the amount of water to be added depends on the type, particle diameter, and the like of the water-absorbing resin precursor.

[0042] The surface cross-linking agent may be added to the water-absorbing resin precursor, for example, when the water-absorbing resin precursor has been dispersed in the hydrophilic organic solvent. The method of mixing them is not particularly limited. Among a variety of mixing methods, it is preferable to employ a method in which (i) the surface cross-linking agent is dissolved, when necessary, in water and/or hydrophilic organic solvent, and (ii) this is sprayed or dropped directly onto the water-absorbing resin precursor. Further, in the case where water is used in the mixing, for example water-insoluble micro particle powder or a surfactant may be added.

[0043] In order to mix the water-absorbing resin precursor and the surface cross-linking agent uniformly and assuredly, it is preferable that a mixing apparatus

having a strong mixing power be used in order to mix the water-absorbing resin precursor and the surface cross-linking agent. Examples of the mixing apparatus include: a circular-tube type mixing apparatus, a double-wall circular cone type mixing apparatus, a V-shape type mixing apparatus, a ribbon type mixing apparatus, a screw type mixing apparatus, a fluidized furnace rotary desk type mixing apparatus, an air-flow mixing apparatus, a two-armed kneader, an internal mixing apparatus, a pulverizing type kneader, a rotary mixing apparatus, and a screw type extruder.

[0044] The water-absorbing resin precursor and the surface cross-linking agent are mixed and then treated with heat. Thereafter, a cross-link is formed in the vicinity of the surface of the water-absorbing resin precursor. It is preferable that the temperature during the heat treatment be in the range of from 160 °C to 250 °C, although the preferable range depends upon which surface cross-linking agent is used. In the case where the heat treatment is performed at a temperature lower than 160 °C, the cross-linking structure is not formed uniformly, and therefore a water-absorbing resin having excellent properties (e.g., absorbency under high pressure) cannot be produced. Thus, this case is not preferable. Further, in the case where the heat treatment is performed at a temperature higher than 250 °C, the water-absorbing resin

precursor is deteriorated. This degrades the properties and the urine-resistibility of the water-absorbing resin. Thus, this case is not preferable, either.

[0045] To perform the heat treatment described above, an ordinarily-used dryer or a heating furnace may be used. For example, a trench type mixing dryer, a rotary type dryer, a desk type dryer, a fluidized bed type dryer, an air-flow type dryer, or an infrared dryer may be used.

[0046] If produced by the above methods, the water-absorbing resin has (i) 36 g/g or greater of absorbency under no pressure with respect to physiological saline, (ii) 24 g/g or greater of the absorbency under high pressure with respect to physiological saline, and (iii) 1 mm/min or less of flow rate at a time when 16 hours have passed since the artificial urine was absorbed. Therefore, the water-absorbing resin of the present invention is suitable not only for paper diapers for babies and sanitary napkins, but also for sanitary material (e.g., diapers for adults) that is to be heavily loaded while being used, which sanitary material has been increasingly demanded.

[0047] It is not certain what causes the water-absorbing resin of the present invention to exhibit (i) significantly excellent urine-resistibility and (ii) high absorbency under both no pressure and high pressure. It is considered that a synergy of the following two factors

contributes thereto. The first factor is that the monomer is polymerized by the aqueous polymerization performed under the presence of the internal cross-linking agent and the phosphorous acid (salt) so that a network having an optimum inter-crosslink molecular weight is formed. The second factor is that the surface of such water-absorbing resin precursor is treated with a particular surface cross-linking agent so that the cross-linking densities in the vicinity of the surface of the water-absorbing resin can be graded.

[0048]

[Examples] The following describes the present invention more specifically, with reference to Examples and Comparative Examples. The present invention, however, is not limited to the description below. The properties of the water-absorbing resin were measured by the methods described later. Further, the word "parts" in the following Examples and Comparative Examples indicates "parts by weight".

[0049] (a) Absorbency under no pressure

First, 0.2 g of water-absorbing resin was evenly put into a tea-bag type pouch (60 mm x 60 mm) made of non-woven fabric, and was soaked in sodium chloride aqueous solution (physiological saline) of 0.9% by weight. When 60 minutes passed, the tea-bag type sac was taken out therefrom and dewatered using a centrifugal separator

with a centrifugal force (250 G) for three minutes. Thereafter, weight  $W_1(g)$  of the tea-bag type pouch was measured. Further, the same process was carried out without using the water-absorbing resin. Thereafter, weight  $W_0(g)$  of the tea-bag type pouch was measured. Then, with weights  $W_0$  and  $W_1$ , the absorbency (g/g) under no pressure was calculated according to the following equation:

Absorbency (g/g) under no pressure

$$= (W_1(g) - W_0(g)) / \text{amount (g) of water-absorbing resin} - 1.$$

[0050]

(b) Absorbency under high pressure

First of all, the following briefly describes a measurement apparatus used for measuring the absorbency under high pressure, with reference to Figure 1.

[0051] As illustrated in Figure 1, the measurement apparatus is constituted of: a balance 1; a container 2 that is placed on the balance 1 and has a predetermined capacity; an external air inlet pipe 3; a conduit pipe 4; a glass filter 6; and a measurement section 5 that is placed on the glass filter 6. The container 2 has an aperture 2a on the top thereof and an aperture 2b on the side face thereof. The external air inlet pipe 3 is inserted into the aperture 2a, and the conduit pipe 4 is mounted in the

aperture 2b. Further, in the container 2, a predetermined amount of physiological saline 12 is stored. A lower end of the external air inlet pipe 3 is soaked in the physiological saline 12. The external air inlet pipe 3 is provided to maintain the pressure in the container 2 at approximately a same level as that in the atmosphere. The glass filter 6 has a diameter of 70 mm. The container 2 and the glass filter 6 are connected to each other by the conduit pipe 4 made of silicone resin. Further, the position and the height of the glass filter 6 is fixed with respect to the container 2.

[0052] Further, the measurement section 5 is provided with: a filter paper 7; a supporting cylinder 9 with an inner diameter of 60 mm; a wire net 10 adhered to a bottom part of the supporting cylinder 9; and a weight 11. In the measurement section 5, the filter paper 7 and the supporting cylinder 9 (in other words, the wire net 10) are placed on the glass filter 6 in the order as listed. Furthermore, the weight 11 is placed on top of the wire net 10, that is, inside of the supporting cylinder 9. The wire net 10 is made of stainless-steel and has 400 meshes (the size of each mesh is 38  $\mu\text{m}$ ). Further, the top surface of the wire net 10 is placed on the same level as the height of the lower end face 3a of the external air inlet pipe 3. In other words, the height of the face of the wire net 10, which face is in contact with the water-absorbing

resin 15, is the same as that of the lower end face 3a of the external air inlet pipe 3. As such, a predetermined amount of the water-absorbing resin 15 is evenly dispersed on the wire net 10. The weight of the weight 11 is 1413 g. This makes it possible to evenly apply a load of 50.0 g/cm<sup>2</sup> with respect to the wire net 10 and therefore to the water-absorbing resin 15.

[0053] With the measurement apparatus structured as described above, the absorbency under high pressure was measured. The following describes the measurement method.

[0054] First of all, predetermined preparatory operations were performed, which preparatory operations include, for example, pouring a predetermined amount of physiological saline 12 into the container 2, and inserting the external air inlet pipe 3 into the container 2. Then, the filter paper 7 was placed on the glass filter 6. Further, concurrently with placing the filter paper 7 on the glass filter 6, (i) 0.9 g of water-absorbing resin was evenly dispersed inside of the supporting cylinder 9, that is, on the wire net 10, and (ii) the weight 11 was placed on top of the water-absorbing resin 15. Thereafter, the supporting cylinder 9 in which the wire net 10, the water-absorbing resin 15, and the weight 11 had been placed on top of the filter paper 7 were placed such that the center of the supporting cylinder 9 coincided with the



center of the glass filter 6.

[0055] Weight  $W_2(g)$  of the physiological saline 12 that was absorbed by the water-absorbing resin 15 in 60 minutes since the supporting cylinder 9 had been placed on top of the filter paper 7 was calculated on the basis of the values measured by the balance 1. Furthermore, the same operations were performed without using the water-absorbing resin 15. The blank weight, that is, the weight of the physiological saline 12 absorbed by a component other than the water-absorbing resin 15 (e.g., filter paper 7) was calculated on the basis of the values measured by the balance 1. The blank value will be referred to as blank value  $W_3(g)$ . Then, weight  $W_2(g)$  was adjusted by using blank value  $W_3(g)$  so as to calculate weight  $W_4(g)$  of the physiological saline that was actually absorbed by the water-absorbing resin in 60 minutes since the beginning of the absorption. Weight  $W_4(g)$  was calculated according to the following formula:

$$W_4(g) = W_2(g) - W_3(g).$$

By using weight  $W_4(g)$  and the weight (0.9 g) of the water-absorbing resin, the absorbency (g/g) under high pressure was calculated according to the following formula:

absorbency (g/g) under high pressure

$$= W_4(\text{g}) / \text{weight (g) of water-absorbing resin.}$$

[0056] (c) Flow rate after artificial urine was absorbed  
First of all, artificial urine was produced. Specifically, 95 g of urea, 40 g of sodium chloride, 5 g of magnesium sulfate, and 4855 g of ion exchanged water were mixed, and then L-ascorbic acid was added at 0.005% by weight. Thereafter, 2 g of water-absorbing resin was placed into a 120 ml-container (inner diameter of 54 mm) having a lid and made of polypropylene. The artificial urine was added to let the water-absorbing resin absorb the artificial urine. As a result, a hydrate gel made of the water-absorbing resin swelled for 25 times larger was produced. The hydrate gel was left in the atmosphere where the temperature was 37 °C and the relative humidity was 90%. Then, when (i) 16 hours passed and (ii) 20 hours passed, the container was leaned 90° to measure the distance the hydrate gel on the lower part of the container moved in one minute. Finally, on the basis of the distance, the flow rate (mm/min) at a time when the artificial urine had been absorbed was calculated.

[0057] (d) Examination of urine-resistibility

In the same manner as the measurement of the flow rate at the time after the artificial urine was absorbed, the water-absorbing resin having absorbed the artificial urine,

or hydrate gel, was left, and after (i) 16 hours passed and (ii) 20 hours passed, the condition of the hydrate gel was visually observed. If the hydrate gel had not been destroyed, then the condition was evaluated as "good". On the other hand, if the hydrate gel had been destroyed, then the condition was evaluated as "poor".

[0058] [Example 1] In the present Example, as a monomer mainly containing acrylic acid and the alkali metal salt thereof, a partially-neutralized sodium acrylic acid (neutralization ratio: 75 mol%) was used. In other words, a mixture (the mixture will be referred to as an acrylic monomer hereinafter) containing the acrylic acid and the sodium acrylic acid at a molar ratio of 1:3 was used. With 5367 g of aqueous solution containing 33% of the partially-neutralized sodium acrylic acid, (i) 5.74 g of polyethyleneglycoldiacrylate (PEGDA) (0.06 mol% with respect to acrylic monomer), acting as a cross-linking agent, and 10.6 g of sodium hydrogen phosphite·2.5hydrate (0.6% by weight with respect to acrylic monomer), acting as phosphorous acid (salt), were dissolved. As a result, a reaction liquid was produced.

[0059] Then, the reaction liquid was supplied into a reactor vessel which was constituted of a lid and a two-armed kneader (content volume of 10 liters) that was made of stainless-steel, was jacketed, and is provided with two sigma blades. While the reaction liquid was

maintained at 26°C, the inside of the system was replaced with nitrogen gas. Thereafter, the reaction liquid was stirred with a blade of the kneader, (i) 12 g of aqueous solution containing 20 % of sodium persulfate and (ii) 10 g of aqueous solution containing 1 % of L-ascorbic acid were added in order to start the polymerization. After the polymerization was performed for 60 minutes, fragmented hydrate gel polymer was produced and taken out therefrom.

[0060] The hydrate gel polymer was spread on the wire net and dried with hot air at 160°C for 60 minutes. The hydrate polymer thus dried was pulverized by a vibrating mill and classified. As a result, a water-absorbing resin precursor whose color was white and particle diameter was 75  $\mu\text{m}$  to 850  $\mu\text{m}$  was produced. The water-absorbing resin precursor had 51 g/g of absorbency under no pressure.

[0061] To 100 parts of the water-absorbing resin precursor, (i) a surface cross-linking agent (0.05 parts of ethyleneglycoldiglycidylether and 0.5 parts of glycerin) and (ii) water solution composed of (a) 3 parts of water and (b) 0.75 parts of isopropyl alcohol were mixed. The mixture was treated with heat at 200°C for 50 minutes. As a result, a water-absorbing resin was produced. With regard to the water-absorbing resin having been produced, (i) the absorbency under no pressure, (ii) the absorbency

under high pressure, and (iii) the gel flow rate (the gel flow rate will be referred to as the property hereinafter) of the water-absorbing resin were measured. These values (the values will be simply referred to as results hereinafter) are shown in Table 1.

[0062] [Example 2] The same reactions as in Example 1 were performed under the same conditions therein, except that 10.6 g of disodium phosphite (0.6% by weight with respect to acrylic monomer), acting as phosphite, was used in place of 10.6 g of sodium hydrogen phosphite·2.5hydrate in Example 1. As a result, a water-absorbing resin precursor was produced. The absorbency of the water-absorbing resin precursor under no pressure was 48g/g. Further, the water-absorbing resin precursor was treated with heat under the same conditions as in Example 1, except that the water-absorbing resin was heated for 45 minutes instead of 50 minutes. As a result, a water-absorbing resin was produced. The properties of the water-absorbing resin were measured. The results of the measurement are shown in Table 1.

[0063] [Example 3] The same reactions and operations as in Example 1 were performed, except that 8.86 g of dipotassium phosphite (0.5% by weight with respect to acrylic monomer), acting as phosphite, was used in place of 10.6 g of sodium hydrogen

phosphite·2.5hydrate in Example 1. As a result, a water-absorbing resin precursor was produced. The absorbency of the water-absorbing resin precursor under no pressure was 50 g/g. Further, the water-absorbing resin precursor was treated with heat under the same conditions as in Example 1 so as to produce the water-absorbing resin. The properties of the water-absorbing resin were measured. The results of the measurement are shown in Table 1.

[0064] [Comparative Example 1] The same reactions and operations as in Example 1 were performed, except that (i) the amount of polyethyleneglycoldiacrylate (PEGDA) was changed to 2.87 g (0.03 mol% with respect to acrylic monomer) from 5.74 g and (ii) sodium hydrogen phosphite·2.5hydrate was not used. As a result, a water-absorbing resin precursor was produced. The absorbency of water-absorbing resin precursor under no pressure was 52 g/g. Then, the water-absorbing resin precursor was treated with heat under the same conditions as in Example 1. As a result, a comparative water-absorbing resin was produced. The properties of the comparative water-absorbing resin were measured. The results of the measurement are shown in Table 1. Note that "the flow rate is more than measurement range" indicates that the hydrate gel was flowed out of the container immediately after the container was leaned, and

therefore the flow rate could not be measured.

[0065] [Comparative Example 2] The same reactions and operations as in Example 1 were performed, except that 0.89 g of sodium hypophosphite·1hydrate (0.05% by weight with respect to acrylic monomer) was used in place of 10.6 g of sodium hydrogen phosphite·2.5hydrate in Example 1. As a result, a water-absorbing resin precursor was produced. The absorbency of water-absorbing resin precursor under no pressure was 52 g/g. Further, the water-absorbing resin precursor was treated with heat under the same conditions as in Example 1, except that the water-absorbing resin precursor was heated for 65 minutes instead of 50 minutes. As a result, a comparative water-absorbing resin was produced. Results of the measurement of the properties of the comparative water-absorbing resin that was produced are also shown in Table 1.

[0066] [Comparative Example 3] In a flask provided with a nitrogen gas inlet tube, 121.4 g of aqueous solution containing 45% by weight of partially-neutralized sodium acrylic acid (neutralization ration: 70 mol%) were supplied. Then, (i) 0.0315 g of N,N-methylenebisacrylamide (0.032 mol% with respect to partially-neutralized sodium acrylic acid), acting as an internal cross-linking agent, and (ii) 0.598 g of disodium phosphite·5hydrate (1.09% with respect to acrylic monomer), acting as phosphorous acid

(salt), were dissolved into the aqueous solution. Further, 0.56 g of hydrogen peroxide 35% solution, acting as polymerization initiator, was added to the aqueous solution. Thereby, a reaction liquid was produced. Then, the inside of the flask was replaced with nitrogen gas so that the reaction liquid was deaerated.

[0067] Further, the dispersion liquid was produced by placing 121 g of cyclohexane and 0.9 g of sorbitanmonostearate in a 500 ml four-necked flask having four apertures, which flask was provided with stirrer, a reflux condenser, a thermometer, and a nitrogen gas inlet tube. The inside of the system was replaced with nitrogen gas. Then, while the temperature of the reaction liquid was maintained in the range of from 55°C to 70°C, a reverse-phase suspension polymerization was performed. The polymerization was finished 60 minutes after the polymerization had started, and thereafter azeotropy dehydration was performed. As a result, a precipitate was generated. The precipitate was filtered to produce a water-absorbing resin precursor.

[0068] Then, 100 parts of the water-absorbing resin precursor that had been produced was mixed with 80 parts of cyclohexane, 0.2 parts of  $\gamma$ -glycidoxypropyltrimethoxysilane, and 0.5 parts of di-n-butyl tin dilaurylate. The mixture was treated with heat at 60°C for 30 minutes, and thereafter at 100°C for



30 minutes. Then, the mixture was dried under reduced pressure. As a result, a comparative water-absorbing resin was produced. The properties of the comparative water-absorbing resin were measured. The results of the measurement are shown in Table 1.

[0069]

[Table 1]

	Absorbency under no pressure (g/g)	Absorbency under high pressure (g/g)	16 hours after artificial urine was absorbed		20 hours after artificial urine was absorbed	
			Visual observation	flow rate (mm/min)	Visual observation	flow rate (mm/min)
EXAMPLE 1	41	26	GOOD	0	GOOD	0
EXAMPLE 2	39	26	GOOD	0	GOOD	0
EXAMPLE 3	40	28	GOOD	0	GOOD	0
COMPARATIVE EXAMPLE 1	40	26	BAD	3	BAD	More than measurement range
COMPARATIVE EXAMPLE 2	41	23	BAD	0-1	BAD	1
COMPARATIVE EXAMPLE 3	69	5.6	BAD	More than measurement range	BAD	More than measurement range

[0070] As it is apparent from the results of Examples 1 to 3 and the results of Comparative Examples 1 to 3, in comparison with the comparative water-absorbing resins,

the water-absorbing resin of the present Examples is excellent in (i) the absorbency under no pressure, (ii) the absorbency under high pressure, and (iii) urine-resistibility.

[0071]

[Effects of the invention] With the above structure, the water-absorbing resin has (i) 36 g/g or greater of absorbency under no pressure with respect to physiological saline, 24 g/g or greater of absorbency under high pressure with respect to physiological saline, and (iii) 1 mm/min or less of flow rate at the time when 16 hours have passed since the artificial urine was absorbed. Thus, the water-absorbing resin is excellent in (i) the absorbency under no pressure, (ii) the absorbency under high pressure, and (iii) the urine-resistibility.

[0072] Accordingly, the water-absorbing resin of the present invention is suitable for paper diapers for babies or sanitary napkins. Furthermore, the water-absorbing resin is also suitable for sanitary materials (e.g., diapers for adults) that are to be heavily loaded while being used, which sanitary material has been increasingly demanded.

[0073] Therefore, in the above method, aqueous polymerization is performed, in the presence of internal cross-linking agent and phosphorous acid and/or its salt, using a hydrophilic unsaturated monomer containing a particular content so as to produce a water-absorbing

resin precursor. Then, a particular surface cross-linking agent is added to the water-absorbing resin precursor, and the mixture is treated with heat. As a result, a water-absorbing resin having the excellent properties described above is produced. Therefore, the above method is suitable for producing the water-absorbing resin.

[Brief description of drawings]

[Figure 1] A cross sectional diagram schematically illustrating a measurement apparatus used for measuring an absorbency under high pressure, which absorbency is one of the properties of the water-absorbing resin of the present invention.

[Explanations of letters or numerals]

- 1 balance
- 2 container
- 3 external air inlet pipe
- 4 conduit pipe
- 5 measurement section
- 6 glass filter
- 7 filter paper
- 9 supporting cylinder
- 10 wire net
- 11 weight
- 12 physiological saline
- 15 water-absorbing resin

**Amendment filed in Japanese Patent Application No.  
286263/1995 (Tokuganhei 7-286263)  
(Publication No. 124710/1997 (Tokukaihei 9-124710))**

**A. Relevance of the Above-identified Document**

The following is a partial English translation of exemplary portions of non-English language information that may be relevant to the issue of patentability of the claims of the present application.

**B. Translation of the Relevant Passages of the Document**

[Claims]

[Claim 1]

A water-absorbing resin produced by (i) performing, in the presence of internal cross-linking agent, aqueous polymerization using a hydrophilic unsaturated monomer so as to produce a water-absorbing resin precursor, the hydrophilic unsaturated monomer mainly containing acrylic acid and/or its alkali metal salt and (ii) adding, to the water-absorbing resin precursor, a surface cross-linking agent that is reactive with a carboxyl group contained in the water-absorbing resin precursor, and treating the mixture with heat, wherein:

the water-absorbing resin has an absorbency of 36 g/g under no pressure where the absorbency under no pressure is measured after soaking the water-absorbing resin in a physiological saline (0.9wt% of sodium chloride aqueous solution) for 60 minutes, and then centrifuging

the water-absorbing resin for 3 minutes by a centrifugal separator at 250 G ( $250 \times 9.81 \text{ m/S}^2$ );

the water-absorbing resin has an absorbency of 24 g/g or greater under high pressure where the absorbency under high pressure is measured after the water-absorbing resin absorbs the physiological saline (0.9wt% of sodium chloride aqueous solution) for 60 minutes while being applied with a load of  $50.0 \text{ g/cm}^2$  (4.90 kPa); and

a hydrogel of the water-absorbing resin has a flow rate of 1 mm/min or below where the flow rate is measured after the hydrogel is left for 16 hours in an atmosphere with a temperature of  $37^\circ\text{C}$  and a relative humidity of 90%, the hydrogel being the water-absorbing resin that has absorbed artificial urine containing 95 g of urea, 40 g of sodium chloride, 5 g of magnesium sulfate, 5 g of calcium chloride, 4855 g of ion-exchanged water, and 0.005wt% of L-ascorbic acid (amount of contents) and consequently has swelled for 25 times larger.

[Claim 2]

A production method of a water-absorbing resin, comprising the steps of (i) performing, in the presence of internal cross-linking agent, aqueous polymerization using a hydrophilic unsaturated monomer so as to produce water-absorbing resin precursor, the hydrophilic

unsaturated monomer mainly containing acrylic acid and/or its alkali metal salt, and (ii) adding, to the water-absorbing resin precursor, a surface cross-linking agent that is reactive with a carboxyl group contained in the water-absorbing resin precursor, and treating the mixture with heat, the method further comprising the step of:

performing, in the presence of phosphorous acid and/or its salt, aqueous polymerization using the hydrophilic unsaturated monomer.

[Claim 3]

The production method as set forth in Claim 2, wherein the internal cross-linking agent is used within the range of from 0.02 mol% to 3 mol% with respect to the hydrophilic unsaturated monomer.

[Claim 4]

The production method as set forth in one of Claims 2 and 3, wherein the phosphorous acid and/or its salt is used within the range of from 0.01 % to 5 % by weight with respect to the hydrophilic unsaturated monomer.

[Claim 5]

The production method as set forth in any one of Claims 2, 3 and 4, further comprising the step of

performing aqueous polymerization using persulfate.

[Claim 6]

The production method as set forth in any one of Claims 2 to 5, wherein:

the water-absorbing resin produced by the method has an absorbency of 36 g/g or greater under no pressure where the absorbency under no pressure is measured after soaking the water-absorbing resin in physiological saline (0.9wt% of sodium chloride aqueous solution) for 60 minutes and then centrifuging the water-absorbing resin for 3 minutes by a centrifugal separator at 250 G (250 x 9.81 m/S<sup>2</sup>);

the water-absorbing resin produced by the method has an absorbency of 24 g/g or greater under high pressure where the absorbency under high pressure is measured after the water-absorbing resin absorbs the physiological saline (0.9wt% of sodium chloride aqueous solution) for 60 minutes while being applied with a load of 50.0 g/cm<sup>2</sup> (4.90 kPa); and

a hydrogel of the water-absorbing resin produced by the method has a flow rate of 1 mm/min or below where the flow rate is measured after the hydrogel is left for 16 hours in an atmosphere with a temperature of 37°C and a relative humidity of 90%, the hydrogel being the water-absorbing resin that has absorbed artificial urine

containing 95 g of urea, 40 g of sodium chloride, 5 g of magnesium sulfate, 5 g of calcium chloride, 4855 g of ion-exchanged water, and 0.005wt% of L-ascorbic acid (amount of contents) and consequently has swelled for 25 times larger.

[Claim 7]

A sanitary material using the water-absorbing resin set forth in Claim 1.

[0012] In order to solve the above problems, a production method of a water-absorbing resin of the present invention, which method includes the steps of (i) performing, in the presence of internal cross-linking agent, aqueous polymerization using a hydrophilic unsaturated monomer so as to produce a water-absorbing resin precursor, the hydrophilic unsaturated monomer mainly containing acrylic acid and/or its alkali metal salt and (ii) adding, to the water-absorbing resin precursor, a surface cross-linking agent that is reactive with a carboxyl group contained in the water-absorbing resin precursor, and treating the mixture with heat, is adapted so that the method further includes the step of performing, in the presence of phosphorous acid and/or its salt, aqueous polymerization using the hydrophilic unsaturated monomer.



[0013] In order to solve the above problems, the production method as set forth in Claim 3 is adapted so that the internal cross-linking agent is used within the range of from 0.02 mol% to 3 mol% with respect to the hydrophilic unsaturated monomer.

[0014] In order to solve the above problems, the production method as set forth in Claim 4 is adapted so that the phosphorous acid and/or its salt is used within the range of from 0.01wt% to 5wt% with respect to the hydrophilic unsaturated monomer.

[0015] In order to solve the above problems, the production method as set forth in Claim 5 is adapted so that the method further includes the step of performing aqueous polymerization using persulfate. Further, in order to solve the above problems, the production method as set forth in Claim 6 is adapted so that: the water-absorbing resin produced by the method has an absorbency of 36 g/g or greater under no pressure where the absorbency under no pressure is measured after soaking the water-absorbing resin in physiological saline (0.9wt% of sodium chloride aqueous solution) for 60 minutes and then centrifuging the water-absorbing resin for 3 minutes by a centrifugal separator at 250 G ( $250 \times 9.81 \text{ m/S}^2$ ); the water-abosrbing resin produced by the method has an absorbency of 24 g/g or greater under high pressure where the absorbency under high pressure is measured

after the water-absorbing resin absorbs the physiological saline (0.9wt% of sodium chloride aqueous solution) for 60 minutes while being applied with a load of 50.0 g/cm<sup>2</sup> (4.90 kPa); and a hydrogel of the water-absorbing resin produced by the method has a flow rate of 1 mm/min or below where the flow rate is measured after the hydrogel is left for 16 hours in an atmosphere with a temperature of 37°C and a relative humidity of 90%, the hydrogel being the water-absorbing resin that has absorbed artificial urine containing 95 g of urea, 40 g of sodium chloride, 5 g of magnesium sulfate, 5 g of calcium chloride, 4855 g of ion-exchanged water, and 0.005wt% of L-ascorbic acid (amount of contents) and consequently has swelled for 25 times larger.

[0017] Further, in order to solve the above problems, the present invention is adapted so that a water-absorbing resin produced by (i) performing, in the presence of internal cross-linking agent, aqueous polymerization using a hydrophilic unsaturated monomer so as to produce a water-absorbing resin precursor, the hydrophilic unsaturated monomer mainly containing acrylic acid and/or its alkali metal salt and (ii) adding, to the water-absorbing resin precursor, a surface cross-linking agent that is reactive with a carboxyl group contained in the water-absorbing resin precursor, and treating the mixture with heat, is adapted so that: the

water-absorbing resin has an absorbency of 36 g/g or greater under no pressure where the absorbency under no pressure is measured after soaking the water-absorbing resin in physiological saline (0.9wt% of sodium chloride aqueous solution) for 60 minutes and then centrifuging the water-absorbing resin for 3 minutes by a centrifugal separator at 250 G ( $250 \times 9.81 \text{ m/S}^2$ ); the water-absorbing resin has an absorbency of 24 g/g or greater under high pressure where the absorbency under high pressure is measured after the water-absorbing resin absorbs the physiological saline (0.9wt% of sodium chloride aqueous solution) for 60 minutes while being applied with a load of  $50.0 \text{ g/cm}^2$  (4.90 kPa); and a hydrogel of the water-absorbing resin has a flow rate of 1 mm/min or below where the flow rate is measured after the hydrogel is left for 16 hours in an atmosphere with a temperature of  $37^\circ\text{C}$  and a relative humidity of 90%, the hydrogel being the water-absorbing resin that has absorbed artificial urine containing 95 g of urea, 40 g of sodium chloride, 5 g of magnesium sulfate, 5 g of calcium chloride, 4855 g of ion-exchanged water, and 0.005wt% of L-ascorbic acid (amount of contents) and consequently has swelled for 25 times larger.











＊〔表1〕

わてて記載した。  
〔0008〕

	高加圧下 吸収倍率 (g/g)	高加圧下 吸収倍率 (g/g)	人工尿吸収後 18時間数値		人工尿吸収後 20時間数値	
			目視	流動速度 (mm/min)	目視	流動速度 (mm/min)
実施例1	4.1	2.6	○	0	○	0
実施例2	3.9	2.6	○	0	○	0
実施例3	4.0	2.8	○	0	○	0
比較例1	4.0	2.6	×	3	×	測定範囲以上
比較例2	4.1	2.3	○	0～1	×	1
比較例3	8.9	5.6	×	測定範囲以上	×	測定範囲以上

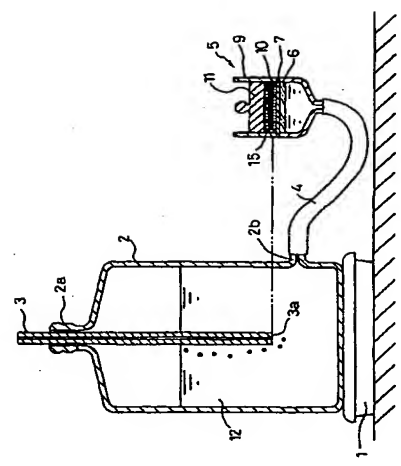
〔0070〕実施例1～実施例3および比較例1～比較例3の結果から明らかなように、本実施例にかかる吸水倍率を製造することができる。従って、上記方法は、吸水性樹脂は、比較用の吸水樹脂と比較して、無加圧下での吸収性能および高加圧下での吸収性能の両方に優れ、しかも耐腐性に優れていることがわかった。

〔0071〕  
〔発明の効果〕上記構成によれば、吸水樹脂は、生理食塩水の無加圧下吸収倍率が36g/g以上、高加圧下吸収倍率が24g/g以上であり、かつ、人工尿吸収後の流動速度が1時間経過後において1mm/min以下である。従って、吸水樹脂は、無加圧下での吸収性能および高加圧下での吸収性能の両方に優れ、しかも耐腐性に優れているという効果を奏する。

〔0072〕従って、本発明の吸水樹脂は、乳幼児用紙オムツや生理用ナプキンに好適であるばかりでなく、近接ニーズが速まりつつある高齢者がかかる大人用オムツ等の衛生材料に好適に用いることができる。

〔0073〕また、上記方法によれば、特定の成分を有する親水性不飽和単量体を、内部架橋剤、および、亜硫酸および/またはその塩の存在下で水溶液混合させて吸水樹脂前駆体を得た後、特定の表面架橋剤を配合して

〔図1〕



フロントページの続き

(72)発明者 塩路 尚武  
兵庫県姫路市網干区西浜字西99番地の  
1 株式会社日本機械内



【公報種別】特許法第17条の2の規定による補正の掲載  
 【部区分分】第3部門第3区分  
 【発行日】平成15年1月15日(2003.1.15)

【公開番号】特開平9-124710

【公開日】平成8年5月13日(1997.5.13)

【年通号数】公開特許公報9-1248

【出願番号】特開平7-286283

【国際特許分類第7版】

C08F 2/10 MAX

A61L 15/00

C08F 6/00 MFR

20/06 M,N

【F1】

C08F 2/10 MAX

6/00 MFR

20/06 M,N

A61F 13/18 307 A

【手続補正書】

【提出日】平成14年10月10日(2002.10.10)

【手続補正1】

【補正対象事項名】明細書

【補正対象項目名】特許請求の範囲

【補正方法】変更

【補正内容】

【特許請求の範囲】

【請求項1】アクリル酸および/またはそのアルカリ金  
 属塩を主成分とする親水性不飽和単量体を、内部架橋剤  
 の存在下で水溶液重合させて吸水性樹脂前駆体を得た  
 後、該吸水性樹脂前駆体が有するカルボキシル基と反応  
 可能な表面架橋剤を混合して加熱処理して得られる吸水性  
 樹脂であって、

生理食塩水(0.9重量%塩化ナトリウム水溶液)中に60  
 分浸漬した後、遠心分離機を用いて250G(250×9.81  
 m/s<sup>2</sup>)で3分間水切りを行ったときの高圧下吸収倍率  
 が36g/g以上、

50.0 g/cm<sup>3</sup>(4.90 kPa)の荷重を加えて生理食塩水(0.  
 9重量%塩化ナトリウム水溶液)を60分間わたって吸  
 水させたときの高圧下吸収倍率が24g/g以上であり、

尿素5%、塩化ナトリウム40%、硫酸マグネシウム5%、  
 塩化カルシウム5%、イオン交換水485%、およびレー  
 スコルビン酸0.005重量%(含有量)からなる人工尿を  
 吸収させることにより25倍に膨潤した含水ゲルとし、こ  
 の含水ゲルを温度37℃、相対湿度90%の雰囲気下で16時  
 間放置した後の含水ゲルの流動速度が1mm/min以下であ  
 ることを特徴とする吸水性樹脂。

【請求項2】アクリル酸および/またはそのアルカリ金

吸収させることにより25倍に膨潤した含水ゲルとし、こ  
 の含水ゲルを温度37℃、相対湿度90%の雰囲気下で16時  
 間放置した後の含水ゲルの流動速度が1mm/min以下であ  
 ることを特徴とする請求項2ないし5のいずれか1項に  
 記載の吸水性樹脂の製造方法。

【請求項7】請求項1記載の吸水性樹脂を用いたことを  
 特徴とする衛生材料。

【手続補正2】

【補正対象事項名】明細書

【補正対象項目名】0012

【補正方法】変更

【補正内容】

【0012】即ち、本発明の吸水性樹脂の製造方法は、  
 上記の課題を解決するために、アクリル酸および/また  
 はそのアルカリ金属塩を主成分とする親水性不飽和単量  
 体を、内部架橋剤の存在下で水溶液重合させて吸水性樹  
 脂前駆体を得た後、該吸水性樹脂前駆体が有するカルボ  
 キシル基と反応可能な表面架橋剤を混合して加熱処理す  
 る吸水性樹脂の製造方法であって、上記親水性不飽和単  
 量体を乾燥後および/またはその塩の存在下で水溶液重  
 合させることを特徴としている。

【手続補正3】

【補正対象事項名】明細書

【補正対象項目名】0013

【補正方法】変更

【補正内容】

【0013】請求項3記載の発明の吸水性樹脂の製造方  
 法は、上記の課題を解決するために、本発明の吸水性樹  
 脂の製造方法において、上記内部架橋剤を、親水性不飽  
 和単量体に対して0.02〜3モル%の範囲内で用いること  
 を特徴としている。

【手続補正4】

【補正対象事項名】明細書

【補正対象項目名】0014

【補正方法】変更

【補正内容】

【0014】請求項4記載の発明の吸水性樹脂の製造方  
 法は、上記の課題を解決するために、本発明の吸水性樹  
 脂の製造方法において、上記樹脂前駆体および/またはその  
 塩を、親水性不飽和単量体に対して0.01〜5重量%の範  
 囲内で用いることを特徴としている。

【手続補正5】

【補正対象事項名】明細書

【補正対象項目名】0015

【補正方法】変更

【補正内容】

【0015】請求項5記載の発明の吸水性樹脂の製造方  
 法は、上記の課題を解決するために、本発明の吸水性樹  
 脂の製造方法において、過硫酸塩を用いて水溶液重合さ  
 せることを特徴とする。請求項6記載の発明の吸水性  
 樹脂の製造方法は、上記の問題を解決するために、本  
 発明の吸水性樹脂の製造方法において、得られる吸水性  
 樹脂が、生理食塩水(0.9重量%塩化ナトリウム水溶  
 液)中に60分浸漬した後、遠心分離機を用いて250G(25  
 0×9.81 m/s<sup>2</sup>)で3分間水切りを行ったときの高圧下  
 吸収倍率が36g/g以上、50.0 g/cm<sup>3</sup>(4.90 kPa)の荷  
 重を加えて生理食塩水(0.9重量%塩化ナトリウム水溶  
 液)を60分間わたって吸水させたときの高圧下吸収  
 倍率が24g/g以上であり、かつ、尿素5%、塩化ナトリ  
 ウム40%、硫酸マグネシウム5%、塩化カルシウム5%、イ  
 オン交換水485%、およびレースコルビン酸0.005重  
 量%(含有量)からなる人工尿を吸収させることにより  
 25倍に膨潤した含水ゲルとし、この含水ゲルを温度37  
 ℃、相対湿度90%の雰囲気下で16時間放置した後の含水  
 ゲルの流動速度が1mm/min以下であることを特徴として  
 いる。

【手続補正6】

【補正対象事項名】明細書

【補正対象項目名】0017

【補正方法】変更

【補正内容】

【0017】また、本発明の吸水性樹脂は、上記の課題  
 を解決するために、アクリル酸および/またはそのアル  
 カリ金属塩を主成分とする親水性不飽和単量体を、内部  
 架橋剤の存在下で水溶液重合させて吸水性樹脂前駆体を  
 得た後、該吸水性樹脂前駆体が有するカルボキシル基と  
 反応可能な表面架橋剤を混合して加熱処理して得られる  
 吸水性樹脂であって、生理食塩水(0.9重量%塩化ナト  
 リウム水溶液)中に60分浸漬した後、遠心分離機を用い  
 て250G(250×9.81 m/s<sup>2</sup>)で3分間水切りを行ったと  
 きの高圧下吸収倍率が36g/g以上、50.0 g/cm<sup>3</sup>(4.90  
 kPa)の荷重を加えて生理食塩水(0.9重量%塩化ナト  
 リウム水溶液)を60分間わたって吸水させたときの高  
 圧下吸収倍率が24g/g以上であり、かつ、尿素5%、  
 塩化ナトリウム40%、硫酸マグネシウム5%、塩化カルシ  
 ウム5%、イオン交換水485%、およびレースコルビン  
 酸0.005重量%(含有量)からなる人工尿を吸収させる  
 ことにより25倍に膨潤した含水ゲルとし、この含水ゲル  
 を温度37℃、相対湿度90%の雰囲気下で16時間放置した  
 後の含水ゲルの流動速度が1mm/min以下であることを特  
 徴としている。